



Degradation of Acid Blue 74 using Fe-ZSM5 zeolite as a heterogeneous photo-Fenton catalyst

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ABSTRACT

Decolourisation and mineralization of an indigoid dye, C.I. Acid Blue 74, was conducted using Fe-ZSM5 zeolite as a catalyst in the presence of UV-C light and H₂O₂. The effects of different parameters such as amounts of catalyst, initial concentration of the dye and H₂O₂ and initial pH of the dye solution on the degradation efficiency of the process were assessed. The results indicated that by using 21.4 mmol l⁻¹ of H₂O₂ and 0.5 g l⁻¹ of the catalyst at pH 5, about 57% total organic carbon of a solution containing 8.56 × 10⁻⁵ mol l⁻¹ Acid Blue 74 could be removed after 120 min in a 2 l batch photo-reactor. Leaching tests indicated that the activity of the catalyst is not due to leached iron ions, although an amount of about 0.3 mg l⁻¹ iron ions was found in the aqueous solution. Significantly lower concentration of Fe²⁺ and Fe³⁺ in the solution after the treatment could give a great advantage to UV/Fe-ZSM5/H₂O₂ system over the homogeneous Fenton-type system. It was found that by using this catalyst, it is possible to expand the range of pH values for which Fenton-type oxidation can occur and no iron hydroxide sludge is formed. It was also observed that catalytic behaviour could be reproduced in consecutive experiments without a considerable drop in the process efficiency.

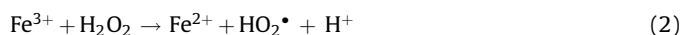
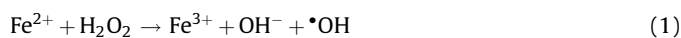
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1. Introduction

Nowadays, colours are inseparable elements of human daily life and they are used in almost all production sectors in industry. Total world dye production is now estimated to be of the order of 700,000 tons per year. A little more than half of the production concentrates on textile dyes and some 15% are used for other substrates dyed in a similar manner to textiles (leather, paper, etc.) [1]. Therefore, production effluents that are normally coloured, are a major source of environmental contamination. The conventional methods used for coloured wastewater purification are biological oxidation and physical–chemical treatment (e.g. coagulation–flocculation, and activated carbon adsorption). These processes are not sufficiently efficient since dyes are hardly removable due to their high-molecular stability and water solubility. Another difficulty with these methods is that they are not destructive and they only transfer the contamination from one phase to another, therefore, a new and different kind of pollution is faced and further treatments are deemed necessary [2,3]. Biological

treatment of wastewater is the most cost-effective alternative compared with other treatment options. Nevertheless, dye-containing effluents are known to contain toxic and/or non-biodegradable organic substances, so biological processes are not efficient in these cases [4]. An attractive, sludge free alternative for the treatment of a wide range of organic pollutants in wastewater, is the use of advanced oxidation processes (AOPs). Hydroxyl radicals (*OH), highly reactive species generated in sufficient quantities by these systems, have the ability to oxidize the majority of organics in industrial effluents [5]. Common AOPs involve Fenton and photo-Fenton processes, ozonation, electrochemical oxidation, photolysis with H₂O₂ and O₃, high-voltage electrical discharge process, TiO₂ photocatalysis, radiolysis, water solution treatment by electronic beams or γ beams and various combinations of these methods [6,7].

Fenton-like processes have been used as a powerful source of hydroxyl radicals from H₂O₂ in the presence of iron cations and mild reaction conditions to treat these effluents [8]. Common homogeneous Fenton processes involve the application of ferrous or ferric salts and hydrogen peroxide in order to produce hydroxyl radical, as shown in the following equations [9]:



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Although these systems offer a cost-effective source of hydroxyl radicals, there are some major drawbacks that limit the industrial application of this technology: (i) the tight range of pH in which the reaction proceeds, (ii) the need for recovering the precipitated catalyst after treatment and (iii) deactivation by some ion-complexing agents like phosphate anions. The resulting sludge may also contain organic substances as well as heavy metals and has to be treated further, thus increasing the overall costs. An alternative method could be the use of heterogeneous solid Fenton catalysts, such as Fe-containing zeolites and clays [10–16]. Heterogeneous photo-Fenton catalysts can diminish the final concentration of iron ions in the bulk after treatment, while by the assistance of UV irradiation the formed Fe^{3+} complexes can be destroyed, allowing Fe^{3+} ions to participate in the Fenton catalytic cycle [17,18]. The use of synthetic zeolites is very promising due to their unique properties [19–21], which could give them an advantage over other carriers (such as clay, laponite, bentonite, etc.) because of their ability to adsorb smaller organic molecules [22,23]. 10-Membered oxygen ring zeolites possess some important characteristic properties including high activity, high tolerance to coking and high-hydrothermal stability. Among the family of 10-membered oxygen ring zeolites, the MFI type (ZSM5) zeolite is probably the most useful one [24].

The goal of this study was to investigate the applicability of Fe-contained synthetic zeolite ZSM5 as heterogeneous photo-Fenton catalyst for minimization of overall organic content in the model wastewater containing an indigoid dye, C.I. Acid Blue 74 (AB74). The effects of different parameters such as catalyst amount, initial concentration of the dye and H_2O_2 and initial pH of the dye solution on the degradation efficiency of the process were assessed. The efficiency of this system was evaluated by determination of total organic carbon (TOC) reduction and concentration of iron ions found in the treated solution.

2. Experimental

2.1. Materials

Indigoid dye C.I. Acid Blue 74 was obtained from Sigma–Aldrich as commercially available dye (85%) and used without further purification. The main characteristics of AB74 are presented in Table 1. Hydrogen peroxide (30%, w/w) was purchased from Prolabo.

2.2. Preparation of Fe-ZSM5

Catalyst Fe-ZSM5 was synthesised according to the general procedure described by Patarin et al. [25], in which fluoride ions are used to solubilize the silica and iron sources. In this procedure, the temperature of synthesis of Fe-ZSM5 is 170 °C. The efficiency of this zeolite in the heterogeneous photo-Fenton process was compared with the one prepared at 90 °C and it was found that due to a bigger crystal size, Fe-ZSM5 prepared at 90 °C is more efficient. So, the sample was prepared at 90 °C and then calcined at

Table 2

Characteristics of Fe-ZSM5 used in this study

Zeolite	Fe-ZSM5
Si/Fe (molar ratio)	29
Unit cell size (Å)	38.95
Surface area (m^2/g)	187

Table 3

Chemical composition (wt%) of Fe-ZSM5 determined by XRF

Chemical compound	wt%	Element	wt%
SiO_2	95.537	Si	44.692
SO_3	0.029	S	0.011
MnO	0.047	Mn	0.036
Fe_2O_3	4.387	Fe	3.070
		O	52.1

550 °C. The starting materials and molar composition of the mixture were:

1SiO_2 ; $0.055\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$; $0.08(\text{C}_3\text{H}_7)_4\text{NBr}$; $0.5\text{NH}_4\text{F}$; $100\text{H}_2\text{O}$

2.3. Characterization of Fe-ZSM5

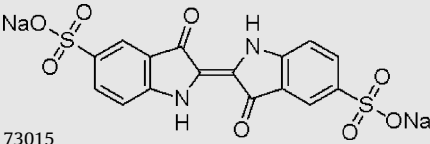
The characteristics of synthesised Fe-ZSM5 are given in Table 2. The chemical composition of this Fe-ZSM5 was determined using a Philips MagiX X-ray fluorescence (XRF) spectrometer and presented in Table 3.

The morphology of the zeolite was studied using Philips XL-30 scanning electron microscopy (SEM). Fig. 1 shows the SEM images of synthesised zeolite and its particle size. It was also checked by powder X-ray diffraction on a STOE STADI-P diffractometer with a linear position-sensitive detector (6° 2θ) in Debye–Scherrer geometry and employing Ge monochromated Cu $\text{K}\alpha_1$ radiation ($\lambda = 1.5406$ Å). This analysis showed that the catalyst had a typical zeolite ZSM5 structure and no amorphous material was present (Fig. 2). Thermal decomposition of organic specie (TPA⁺) occluded in the Fe-ZSM5 structure, shows essentially two endothermic peaks at 431 and 459 °C, corresponding to a Si/Fe molar ratio of the starting mixture smaller than 30. Patarin et al. [25] have studied iron distribution within the crystals of zeolite by X-ray emission mapping of iron. They have concluded that the crystals show an iron-rich core and a silicon-rich outer shell.

2.4. Photo-reactor and procedures

In this work, a cubic batch photo-reactor with an UV lamp (Philips, 15 W, 253.7 nm) in the centre was employed (Fig. 3). To

Table 1
Chemical structure and characteristics of Acid Blue 74

Chemical structure	
	
C.I. number	73015
$\epsilon_{\lambda_{\text{max}}}$ ($\text{l mol}^{-1} \text{cm}^{-1}$)	19.15×10^3
λ_{max} (nm)	610
Chemical class	Indigoid
Mw (g mol^{-1})	466.35

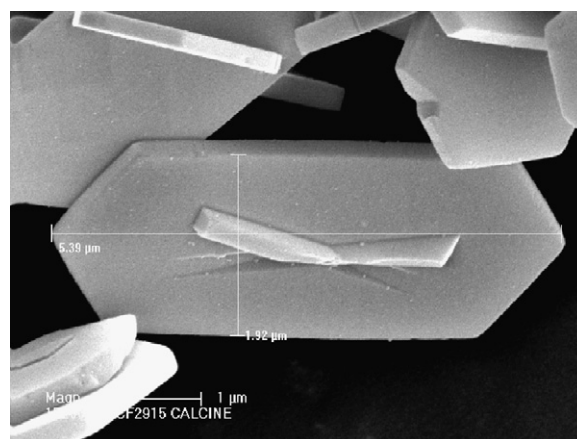


Fig. 1. SEM image of zeolite Fe-ZSM5 synthesised at 90 °C and then, calcined at 550 °C.

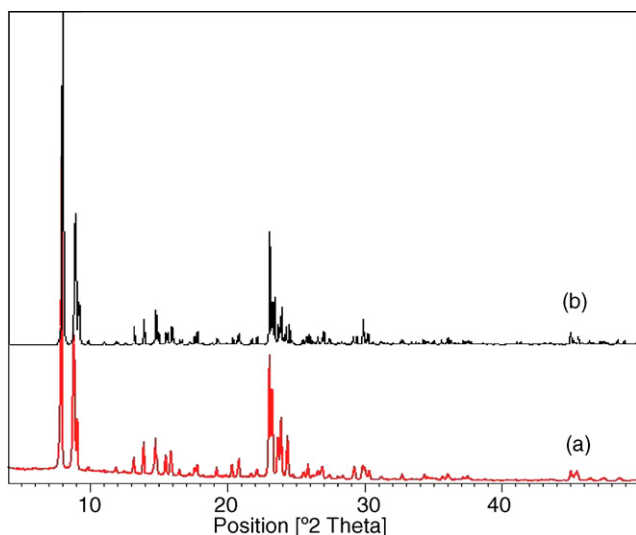


Fig. 2. XRD patterns of (a) synthesised Fe-ZSM5 and (b) a typical zeolite ZSM5.

effectively suspend the zeolite particles in the reactor, two magnetic stirrers were employed. The reactor was equipped with two electrodes for monitoring of pH and temperature. The radiant flux of this lamp was determined by means of a chemical actinometer: hydrogen peroxide. The incident photon flux was estimated at 1.09×10^{-5} einstein s^{-1} .

In every run, 2 l of solution with the desired concentration of the dye and the Fe-ZSM5 load were fed into the reactor. The suspension was magnetically stirred. The pH of the solution was adjusted using dilute chloridric acid or aqueous sodium hydroxide solutions. After 60 min of premixing, a defined content of H_2O_2 was added to the mixture and the lamp was switched on to initiate the reaction. At regular time intervals, samples were taken and filtrated with a $0.45\text{-}\mu\text{m}$ filtration paper and then analysed by UV–vis spectrophotometer and TOC analyser. In the all experiments, the temperature of the solution increased about $7\text{--}8^\circ\text{C}$ during the process, while the initial temperature was room temperature.

2.5. Analyses

The visible light absorbance at the characteristic wavelength of the dye solution, i.e. 610 nm, was recorded to follow the progress of the decolourisation during the process. UV–vis absorption spectras were recorded using a JASCO (V-530) UV–Vis spectrophotometer. The extent of mineralization of the dye was determined on the basis of total organic carbon measurements using a Shimadzu TOC-V_{CSN} analyser.

Decolourisation and mineralization efficiencies were calculated by following expressions:

$$\text{Decolourisation efficiency (\%)} = \left(1 - \frac{[\text{AB74}]}{[\text{AB74}]_0}\right) \times 100 \quad (3)$$

$$\text{Degradation efficiency (\%)} = \left(1 - \frac{[\text{TOC}]}{[\text{TOC}]_0}\right) \times 100 \quad (4)$$

where $[\text{AB74}]_0$ and $[\text{TOC}]_0$ are the initial concentration (mg l^{-1}) of the dye and TOC, respectively. $[\text{AB74}]$ and $[\text{TOC}]$ are the same parameters at time t .

The concentrations of iron ions in the treated solution were determined by colorimetric methods using the UV–vis spectrophotometer. Ferrous ions were identified by the reaction of Fe^{2+} with 1,10-phenanthroline giving orange-red complex ($\lambda_{\text{max}} = 510\text{ nm}$),

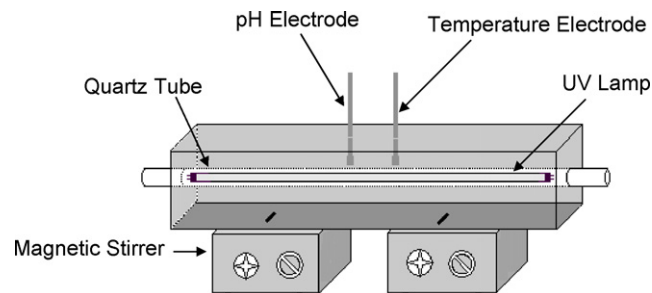


Fig. 3. Batch photo-reactor equipped with a 15-W lamp.

while ferric ion concentration was determined by the reaction of Fe^{3+} with thiocyanate forming a red-coloured complex ($\lambda_{\text{max}} = 480\text{ nm}$) under acidic conditions [26].

3. Results and discussion

3.1. Decolourisation

Decolourisation of Acid Blue 74 dye solution by photo-Fenton type process using Fe-ZSM5 as a heterogeneous catalyst was performed successfully and more than 99% of decolourisation efficiency obtained in all cases within 10 min of the treatment (Fig. 4). It has been found that addition of zeolite without application of $\text{UV}/\text{H}_2\text{O}_2$ shows no changes in UV–vis spectra of the dye solutions, even after 24 h of treatment. Therefore, it could be concluded that adsorption of the dye molecules onto zeolite particles does not play a significant role in the decolourisation process.

3.2. Mineralization

The photocatalytic activity of Fe-ZSM5 for mineralization of AB74 dye in the presence of hydrogen peroxide was studied in detail. The effect of important reaction parameters was investigated.

3.2.1. Effect of hydrogen peroxide concentration

Hydrogen peroxide concentration is an important parameter for the degradation of the dye in the heterogeneous photo-Fenton reactor. Indeed, two opposing factors must be considered:

- (1) If large quantities of H_2O_2 are added to the solution, the fraction of light absorbed by the photo-decomposition promoter, and consequently its photolysis rate, increases. So, more hydroxyl radicals are available for the dye oxidation.
- (2) OH radicals efficiently react with hydrogen peroxide (Eq. (5)), so that H_2O_2 in excess contributes to the $\cdot\text{OH}$ -scavenging

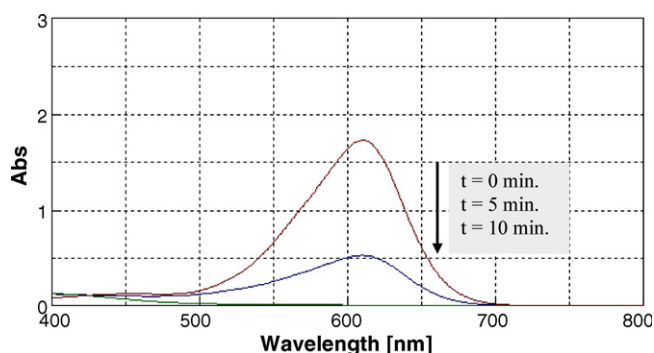


Fig. 4. Variation of the dye solution spectral during the process in optimum condition (initial concentration of the dye = $8.56 \times 10^{-5}\text{ M}$, hydrogen peroxide dosage = 21.4 mM , concentration of the catalyst = 0.5 g l^{-1} and pH 5.2).

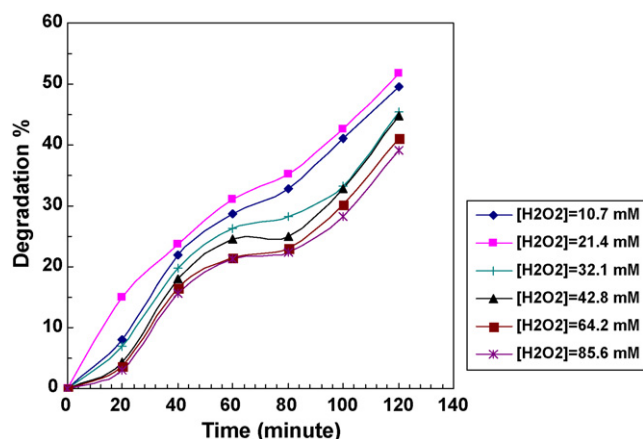


Fig. 5. Effect of concentration of H_2O_2 on degradation efficiency of the process (initial concentration of the dye = 8.56×10^{-5} M, concentration of the catalyst = 0.5 g l^{-1} and pH 5.2).

capacity and reduces the efficiency of pollutant degradation [5].



Note that $\text{HO}_2\cdot$ is less reactive than $\cdot\text{OH}$, with reaction rate constants lower than $2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ in the presence of organic matter, leading therefore to negligible contribution to the dye degradation [27]. At low concentration, H_2O_2 cannot generate enough hydroxyl radicals and the oxidation rate is logically slow. Furthermore, most of the free radicals are directly consumed by the dye. In the presence of high concentration of H_2O_2 , we could expect that more OH radicals would be produced. However, these radicals preferably react with the excess of H_2O_2 . This undesirable reaction competes with the degradation of the dye. Therefore, an important step in the optimization of the method is the determination of the adequate amount of H_2O_2 , to avoid an excess amount of reagent that can postpone degradation. The results showed in Fig. 5 point out the negative effect of a defect or excess amount of H_2O_2 on the process efficiency. An optimum value of about 21.4 mmol l^{-1} for the hydrogen peroxide concentration was obtained when the initial concentration of the dye was $8.56 \times 10^{-5} \text{ mol l}^{-1}$ and the initial pH 5.2 (natural pH of the dye solution). Neamtu et al. [10] have reported that H_2O_2 dosage more than 20 mmol l^{-1} corresponds to an unprofitable consumption of H_2O_2 in the Fe-exchanged/ H_2O_2 process used for the decolourisation of reactive yellow dye.

3.2.2. Influence of the catalyst concentration

The influence of the catalyst concentration on degradation efficiency versus time is presented in Fig. 6. The efficiency of the heterogeneous photo-Fenton process increased with an increase in the amount of catalyst, reached the higher value (0.50 g l^{-1} of the catalyst) and then decreased. The reason for this decrease is thought to be the fact that when the concentration of the catalyst rises, the solid particles increasingly block the penetration of the photons so the overall number of the photons that can be reached to H_2O_2 molecules decreases. Consequently, the efficiency of production of OH radicals decreases. Li et al. [28] have reported the same content of catalyst Al/F-Bentonite for discolouration of a solution containing azo dye X-3B in a photo-Fenton process. They have explained that an increase of the Al/Fe-B catalyst loading will increase the amount of Fe ions involved in the photo-Fenton

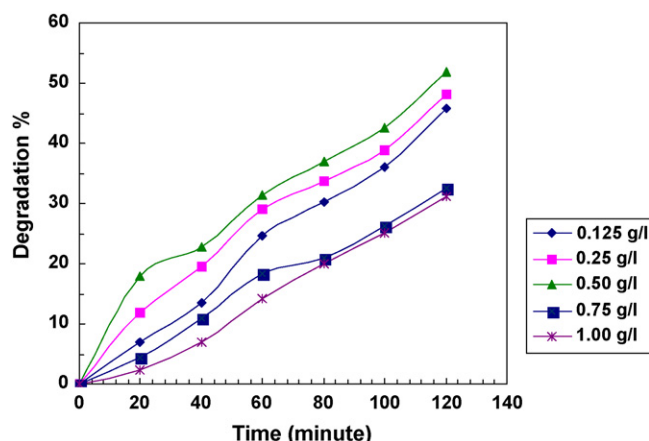


Fig. 6. Effect of the catalyst concentration on degradation efficiency of the process (initial concentration of the dye = 8.56×10^{-5} M, hydrogen peroxide dosage = 21.4 mM and pH 5.2).

process, which in turn increase the number of hydroxyl radical. But, the solution will become more turbid as the catalyst dosage increases, which will decrease the penetration of UV light and the number of hydroxyl radicals.

3.2.3. Effect of initial pH of the solution

The influence of initial pH of the dye solution on the UV/Fe-ZSM5/ H_2O_2 process efficiency was studied using five solutions with pH values determined initially (about 3, 4, 5, 6 and 8) and without any modifications or control of pH during the process. In Fig. 7, the obtained results for dye degradation as a function of the initial pH of the solution at various reaction times are presented. It can be seen in Fig. 8, as the process proceeded, the fragmentation of organic material into organic acids led to a drop of pH. In the case of pH 5 (natural pH of the solution), pH decreased from 5.0 to about 3.5 during the reaction time-span, whereas for experiments done at pH 8, the pH dropped from 8 to 3.8. At pH 3, the pH value remained unchanged during the treatment. It seems that acidic condition conducts to an acceleration of the degradation reaction kinetics. About 57% of the dye mineralization was achieved after 120 min of the photocatalytic treatment at pH 5. This observation is important since it is well known that one major drawback of homogeneous photo-Fenton is the tight range of pH. The activity of the catalyst at pH 5 could be related to the particular environment

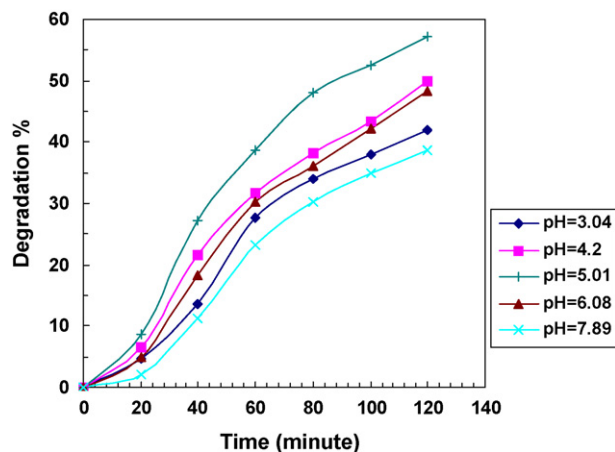


Fig. 7. Effect of initial pH of the solution on degradation efficiency of the process (initial concentration of the dye = 8.56×10^{-5} M, hydrogen peroxide dosage = 21.4 mM and catalyst concentration = 0.5 g l^{-1}).

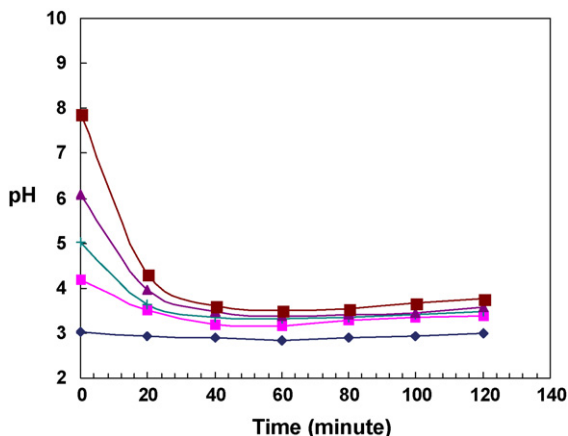
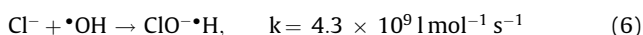


Fig. 8. Variation of pH of the dye solution during the process (initial concentration of the dye = 8.56×10^{-5} M, hydrogen peroxide dosage = 21.4 mM and catalyst concentration = 0.5 g l^{-1}).

of Fe cations inside the pore structure of the zeolite, where strong electrostatic fields are present. The distribution of iron species in this environment has not been elucidated yet, but it is believed that it depends strongly on the pH of the solution [10]. It seems that the interaction of Fe^{3+} with the negatively charged zeolite framework can prevent or slow down the precipitation of iron hydroxides, even at quasi-neutral pH values. An appropriate distribution of the negative charge over the zeolite framework appears to be the key factor that controls the activity of iron species as a function of pH [8]. As the rate of dye mineralization directly depends on hydrogen peroxide photolysis, the decrease of process efficiency in the initial acidic and alkaline conditions can be also explained by considering the following parameters [29]:

- (1) In the initial acidic pHs, concomitant with acidification of the solution by HCl, a high amount of conjugated base is added to the solution. The anion Cl^- is able to react with hydroxyl radicals leading to inorganic radical ions (Eq. (6)).



These inorganic radical anions show a much lower reactivity than $\cdot\text{OH}$, so that they do not take part in the dye mineralization. There is also a drastic competition between the dye and anions with respect to $\cdot\text{OH}$.

- (2) At alkaline pHs, the amount of conjugate base of H_2O_2 increases (Eq. (7)).



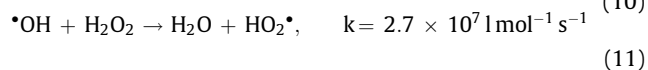
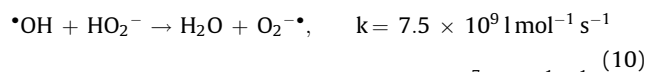
HO_2^- has a higher cross-section (240 mol cm^{-1}) than H_2O_2 (18.6 mol cm^{-1}) at 254 nm, which favours the absorption of UV by HO_2^- and should normally increase the $\cdot\text{OH}$ production (Eq. (8)).



But HO_2^- , the conjugate anion of H_2O_2 , reacts with a non-dissociated molecule of H_2O_2 according to Eq. (9) which leads to oxygen and water, instead of hydroxyl radicals under UV radiation. Therefore, the instantaneous concentration of $\cdot\text{OH}$ is lower than expected.



Furthermore, the deactivation of $\cdot\text{OH}$ is more important when pH of the solution is high. The reaction of $\cdot\text{OH}$ with HO_2^- is approximately 100 times faster than its reaction with H_2O_2 .



The reactivity of $\text{O}_2^-\cdot$ and $\text{HO}_2\cdot$ with organic pollutants is very low compared to that of H_2O_2 [28].

- (3) The self-decomposition rate of hydrogen peroxide (Eq. (12)) strongly depends on pH.



In practice, H_2O_2 is supplied in slightly acid condition (pH 5) for the sake of its high self-decomposition rate at high pHs. The first-order reaction rate constant of this self-decomposition was determined to be 2.29×10^{-2} and $7.40 \times 10^{-2} \text{ min}^{-1}$ at pH 7 and 10.5, respectively.

3.2.4. Effect of initial concentration of the dye

The efficiency of heterogeneous photo-Fenton process as a function of initial concentration of the dye was evaluated. As the lifetime of hydroxyl radicals is very short (only a few nanoseconds), they can only react where they are formed. Increasing the

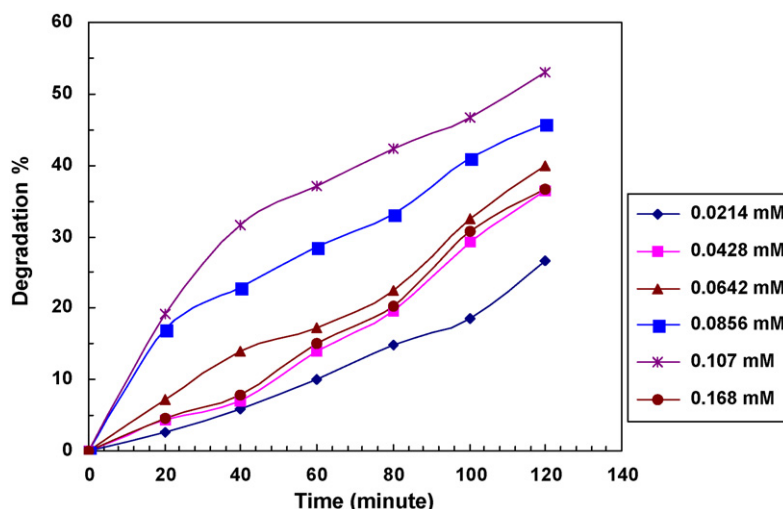


Fig. 9. Effect of initial concentration of the dye on degradation efficiency of the process (hydrogen peroxide dosage = 21.4 mM, catalyst concentration = 0.5 g l^{-1} and pH 5.2).

Table 4

Degradation of AB74 by multi-run experiments in the optimum conditions

Consecutive experiments	Degradation (%)
First run	51.28
Second run	49.55
Third run	48.43

quantity of AB74 molecules per volume unit logically enhances the probability of collision between organic matter and oxidizing species, leading to an increase in the degradation efficiency. But on the other hand, the molar extinction coefficient of the dye at 253.7 nm is very high ($18.7 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$), so a rise in its concentration induces an inner filter effect and incident light would largely be wasted for dye excitation rather than for the hydroxyl radical precursor excitation. Consequently, the solution becomes more and more impermeable to UV radiations. As the rate of hydrogen peroxide photolysis directly depends on the fraction of incident light absorbed by H_2O_2 molecules, the degradation rate slows down. In fact, both above-mentioned opposing phenomena are responsible for the shape of the curves representing the effect of initial concentration of the dye on the process efficiency (Fig. 9).

3.2.5. Leaching and stability tests

Leaching tests were carried out to check the potential of leaching of iron ions from zeolite, and involved analysis of the solution by colorimetric methods. In this case, the solid was filtered at the temperature of the catalytic reaction, in order to prevent the possible readsorption. This method allowed direct determination of the presence of iron ions in solution. In all of the experiments, concentration of the Fe^{2+} and Fe^{3+} ions were below 0.3 mg l^{-1} . This shows that catalysis is mainly due to heterogeneous catalyst (Fe-ZSM5) and not to the leached iron ions, even though a small amount of iron was found in the aqueous solution. The same observation was reported by Centi et al. [9] for the catalytic wet peroxide oxidation of carboxylic acids.

Apart from the photo-catalytic activity of the catalyst in the heterogeneous photo-Fenton process, another important property is its long-term stability. In order to test the long-term stability of the catalyst, zeolite recovered by filtration from the solution after treatment, was washed with ultra-pure water, dried at 110°C (overnight) and then tested again under the same reaction conditions. As can be seen in Table 4, the catalytic behaviour of

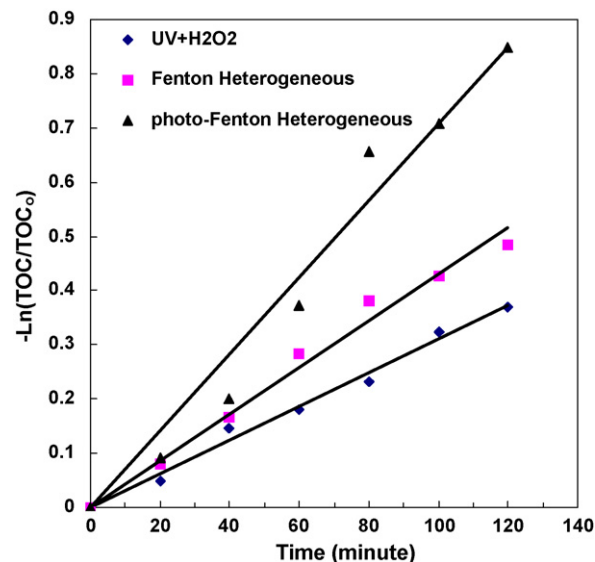


Fig. 11. Comparing of the kinetics of three studied processes: ($k(\text{UV}/\text{H}_2\text{O}_2) = 3.1 \times 10^{-3} \text{ min}^{-1}$; $k(\text{Fe-ZSM5}/\text{H}_2\text{O}_2) = 4.3 \times 10^{-3} \text{ min}^{-1}$; $k(\text{UV}/\text{Fe-ZSM5}/\text{H}_2\text{O}_2) = 7.1 \times 10^{-3} \text{ min}^{-1}$).

Fe-ZSM5 could be reproduced in consecutive experiments without a considerable drop in the process efficiency, indicating the absence of significant deactivation, either due to the small loss of iron or to in situ transformation of the catalyst.

In addition, FT-IR spectra of the catalyst (Zeolite Fe-ZSM5) before and after the treatment process were recorded (Fig. 10). It could be seen that there was no change in the chemical structure of the zeolite after the treatment process.

Finally, assuming that first-order degradation occurs during heterogeneous photo-Fenton, the kinetics of the UV/Fe-ZSM5/ H_2O_2 process in the optimum conditions (initial concentration of the dye = $8.56 \times 10^{-5} \text{ mol l}^{-1}$, hydrogen peroxide dosage = 21.4 mmol l^{-1} , catalyst concentration = 0.5 g l^{-1} and pH 5.2) was compared with that of the UV/ H_2O_2 and Fe-ZSM5/ H_2O_2 systems. As shown in Fig. 11, the UV/Fe-ZSM5/ H_2O_2 was the most efficient process for the degradation of a dye solution containing Acid Blue 74. This could be explained by the fact that the presence of UV radiation not only increases the formation of OH radicals by photolysis of H_2O_2 , but also runs the photo-reduction of Fe(III) to Fe(II) ions, a step that produces new OH radicals and regenerates Fe(II) ions that can further react with more H_2O_2 molecules.

4. Conclusion

In a batch UV/Fe-ZSM5/ H_2O_2 process used for the degradation of an indigoid dye (C.I. Acid Blue 74), catalyst and H_2O_2 concentration, initial concentration of the dye and initial pH of the dye solution are important variables on the process efficiency. Under optimal conditions (pH 5, 21.4 mmol l^{-1} of H_2O_2 and 0.5 g l^{-1} of the catalyst), 57.14% TOC of a solution containing $8.56 \times 10^{-5} \text{ mol l}^{-1}$ Acid Blue 74 could be removed after 120 min in a 2 l photo-reactor. Leaching tests indicated that the activity of the catalyst is not due to leached iron ions, although an amount of about 0.3 mg l^{-1} of these ions was found in aqueous solution. Significantly lower concentration of iron ions in the solution after the treatment could give this system, UV/Fe-ZSM5/ H_2O_2 , a great advantage over the homogeneous Fenton-type system. It was found that using this catalyst, it is possible to expand the range of pH values for which Fenton-type oxidation can occur and no iron hydroxide sludge is formed. It was also observed that catalytic behaviour could be reproduced

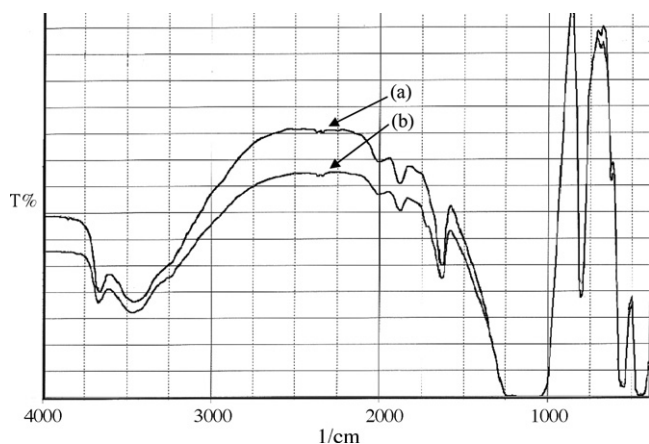


Fig. 10. FT-IR spectra of the zeolite: (a) before treatment and (b) after treatment in the optimum conditions of the process.

in consecutive experiments without a considerable drop in the process efficiency.

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